CHARACTERIZATION OF THE KENICS MIXER AS A LIQUID-LIQUID EXTRACTIVE REACTOR

Conventional liquid-liquid contacting equipment is not completely satisfactory for conducting solvent extraction of metals because slow reaction rates limit process efficiency. The efficiency of copper extraction with Kelex 100 in a Kenics mixer is investigated and analyzed in terms of interfacial areas and intrinsic reaction kinetics obtained from single-drop experiments. The area factor varies with total flow rate such that conversion increases with throughput in the differential reactor studied.

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The industrial importance of processes requiring the contact of two liquid phases is in sharp contrast with the level of development of procedures which permit their efficient design. Methods for equipment design for these two-phase reactors are generally far less satisfactory than those for, say, distillation or homogeneous chemical reaction. The lack of ability to design two liquid phase contacting equipment efficiently is particularly apparent in the liquid-liquid extraction of metals, a field which has become increasingly important in recent years. These extractions frequently involve a multicomponent heterogeneous reaction, and this introduces substantial complications into the design problem.

The application of liquid-liquid extraction to the recovery of copper from aqueous leach liquors has attracted considerable commercial interest. Although process applications look like conventional solvent extraction, the extraction rate for this system is limited by a slow, heterogeneous chemical reaction (*1*), and the corresponding design problem is more properly viewed in terms of chemical reactor design. Commercial applications have used specific chelating agents which react with the aqueous metal according to the stoichiometry.

$$Cu^{2+} + 2HR \rightleftarrows CuR_2 + 2H^+ \qquad (1)$$

The extractant HR and metal-extractant complex CuR_2 are insoluble in water and are carried in an inert organic diluent. The reaction occurs at the interface between the two phases.

The slow rate of this extraction limits the efficiency of conventional liquid-liquid contracting equipment. A possible alternative contactor for this extraction is a static mixer, a plug-flow-like reactor with concurrent flow of the two phases and continuous turbulent mixing. Besides the possibility of higher average transfer rates than in a stirred-tank reactor, such a configuration should offer greater opportunity for exploiting the kinetic selectivity of the extraction reagent. We have investigated the efficiency of copper extraction by Kelex 100, a patented chelating agent sold commercially by Ashland Chemical Company, in such a reactor.

THE ROLE OF EXPERIMENTATION IN CHARACTERIZING THE REACTOR

In a practical contactor, the progress of a metal extraction such as Equation (1) is governed by a complex set of physical and chemical phenomena. In the case of copper extraction by Kelex 100, the rate of reaction (1) has been found to depend in a complicated manner on the interfacial concentrations of copper, acid, and reagent, and the physical situation within the reactor is complicated both by the surfactant nature of the extraction agent (Kelex 100 is a substituted hydroxyquinoline) and by impurities likely to be present in any commercial leach liquor. In view of these complexities, it is reasonable to assume that reactor models which are useful for equipment design purposes will contain unknown parameters whose values must be estimated from experimental data. The reactor should be modeled in a manner that makes efficient use of this experimental effort.

Let us consider a plug-flow reactor with organic-phase volume fraction ϕ and interfacial area per unit dispersion volume a. A material balance on the metal in the aqueous

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phase gives

$$\frac{dc_M}{d\zeta} = -\frac{\tau a}{1-\phi} N_M \qquad (2)$$

For extractions such as copper extraction by Kelex 100 which are limited by slow, heterogeneous chemical reaction, one would expect the flux N_M to be a function of the concentrations of the species involved in the reaction:

$$N_M = k \cdot f(c) \qquad (3)$$

Where k is a proportionality constant. Thus, the design equation can be written as

$$\frac{dc_M}{d\zeta} = -\frac{\tau a}{1-\phi} kf(c) \qquad (4)$$

Traditionally, investigators have sought to develop correlations for k and a separately. The motivation for this is that the two quantities depend principally on different phenomena: the reaction-rate constant k depends on the chemical kinetics involved, whereas the specific interfacial area depends primarily on the reactor configuration and the Weber number. Nevertheless, this approach may not be appropriate for complicated chemical systems such as are encountered in hydrometallurgy. For these systems, difficulties arise in the independent measurement of either of these two quantities.

First, the measurement and correlation of rate data for liquid-phase reactions limited by heterogeneous chemical kinetics is complicated by the occurrence of interfacial phenomena, such as interfacial turbulence and the formation of interfacial films. For example, for the copper-Kelex 100 system, Bauer (*1*) found that metal extraction fluxes measured in a stagnation point flow cell, which had an aged interface, were slower by an order of magnitude than those measured in a growing drop cell, where the interface was continuously renewed. Bauer showed that reproducible metal extraction rates could be measured using the growing drop cell; there is some question, however, whether the specific rate data collected using the growing drop cell are representative of the rates actually occurring in process equipment. This is because his growing drop cell had two surfaces across which transfer can occur: the interface between the growing drop and the continuous phase and the interface in the reservoir which receives the fallen drop. The interface of the growing drop is renewed in a different manner than the reservoir interface. In view of the very slow rates observed in the stagnation-point flow cell, the assumption that both interfaces are equally active for the reaction is unsatisfactory. Uncertainties in determining the interfacial area effective for transfer and relating it to the effective area in actual contacting equipment seem likely to plague any experimental technique for measuring the absolute extraction rate. On the other hand, the collection of rate data with the growing drop cell is simpler than with bench scale reactor models, and the kinetic model from the growing drop cell should be accurate except for a multiplicative constant of order unity. Thus, it should be appropriate to use data from the growing drop cell to identify the functional form as well as the magnitude of the reaction rate.

Second, direct measurement of the interfacial area is at best laborious, and, furthermore, the correlation for predictive purposes of the interfacial area in terms of physical properties and equipment parameters is likely to be very difficult because of the large effect interfacial phenomena can have on dispersion behavior. In the absence of meaningful predictive correlations for the interfacial area, the measurements would have to be repeated for each application.

There thus appears to be little advantage in attempting the independent correlation of the reaction-rate constant and the specific interfacial area. Alternatively, the product (ka) may be viewed as a volumetric rate constant which is characteristic of the local hydrodynamic behavior in the reactor as is commonly done with mass transfer in packed columns. In view of the situation outlined above, it seems reasonable to characterize the reactor in terms of such a combined rate constant rather than in terms of its separate components. In addition to information on the hydrodynamic behavior within the reactor, this volumetric rate constant would also contain information about the chemical kinetics that could not be practically obtained outside of the reactor environment. Given the functional form and magnitude of the reaction rate, say from experiments with the growing drop cell, one can presumably estimate this volumetric rate constant by measuring the fractional conversion in a bench scale, differential model of the particular reactor under consideration. This approach will be successful in so far as it provides for a more efficient use of experimental effort than would be obtained by attempting to describe the system in a more detailed fashion.

The characterization of the reaction for a specific metal extraction system would proceed as follows. First, the intrinsic reaction kinetics are obtained from experiments performed independently of the reactor. The resulting correlation is expected to be accurate except for a multiplicative constant of order unity, but it is recognized that it would be very difficult to obtain a more accurate representation of the reaction rate. Second, the model of the intrinsic reaction rate is coupled with conversion measurements in a differential reactor to estimate a volumetric rate constant which is primarily representative of the hydrodynamic behavior within the reactor. It remains to identify and describe important nonideal mixing effects in the reactor. These nonidealities might arise from deviations from a plug-flow residence-time distribution or from the effects of drop interactions. The identification and modeling of nonideal mixing effects requires experiments with an integral reactor.

EXPERIMENTAL APPARATUS AND PROCEDURE

We have selected the Kenics Static Mixer® as a reactor which should exhibit approximately plug-flow behavior for the concurrent flow of two liquid phases. The Kenics mixer consists of a series of short helical

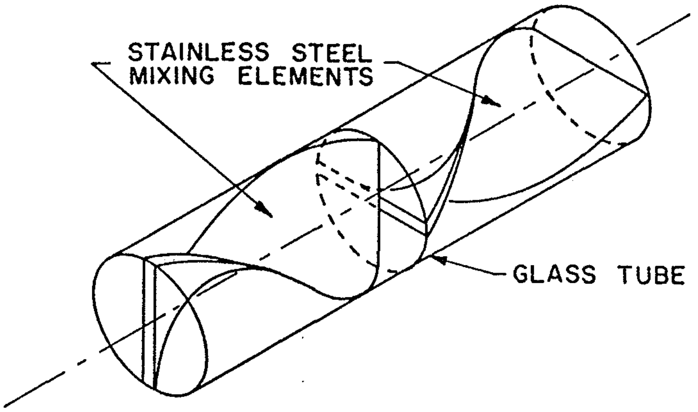


Fig. 1. Mixing elements of a Kenics Static Mixer®.

scan

elements fixed inside a conduit; Figure 1 shows a segment of the contactor containing two of the elements. Each element is a 180 deg section of a left- or right-hand helix which has a pitch such that the length of an element is 1.5 times its width. The elements are alternated and placed with their leading and trailing edges at 90 deg angles. ~~The particular mixer~~ used in the experiments consists of 316-stainless steel mixing elements enclosed in a $\frac{1}{4}$ in. ID glass tube. Contactors similar to the Kenics mixer have been found effective in promoting mass transfer in single-phase flow (*12, 10, 11*) and in the mixing and transportation of small solid particles (*5, 6*). Hazen (*8*) has reported promising results on the use of the mixers for the liquid-liquid extraction of metals.

Figure 2 is a flow sheet of the experimental apparatus. The feed and product reservoirs are 5 gal glass carboys. The feed streams pass from the feed carboys through 8 mm glass tubing to magnetically driven centrifugal pumps and through rotameters before being introduced into the reactor. The two phases are mixed just at the inlet of the reactor and then pass through the reactor to the settler where they separate before exiting to the product carboys. The settler consists of a 75 mm ID glass tube tapered to 8 mm at the inlet end and fitted with outlet lines and Teflon stopcocks at the outlet end. The settler provides about 100 times the residence time of the reactor. This was more than sufficient to separate the phases in the experiments described below.

All of the connecting tubing in the apparatus is 8 mm glass tubing; connections in this tubing were made as required using tubing fittings made of Kynar, a fluorinated hydrocarbon. In addition to the glass tubing and stainless steel mixing elements in the reactor, the organic phase contacts only Teflon and the poly(phenylene sulfide) pump head and impeller. The pump used for the aqueous phase is identical to the organic-phase pump except for the use of a Viton o-ring in the pump head. Viton o-rings are also used in the aqueous rotameter. Flow control is provided by a Teflon flow-control valve on the organic stream and a stainless steel needle valve on the aqueous side.

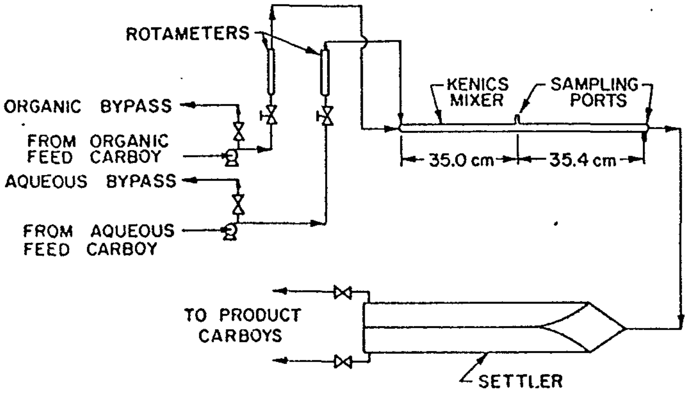


Fig. 2. Flow sheet of experimental apparatus.

Lab Set-Up 9

In all of the experiments that were conducted, the organic phase was either AR-grade xylene or solutions of Kelex 100 in xylene. In these experiments, a steady, homogeneous flow could be maintained in the reactor for organic-phase volume fractions from about 0.1 to 0.9. Slug flow occurred outside this range of volume fractions. Within this range, the organic phase was always the dispersed phase. The inability to operate the equipment with the aqueous phase dispersed may be related to surface wetting effects within the reactor. Such effects would be magnified by the large surface-to-volume ratio in the relatively small reactor used here.

Photographs of the dispersion were taken at various distances from the inlet of the reactor and subsequently analyzed to determine the average drop size. Figure 3 is an example of one of these photographs; one division on the scale in the photograph is equal to 1 mm. The data shown in Table I indicate that there exists a definite entrance region at the beginning of the reactor and that the entrance effects have subsided before the midpoint of the reactor is reached. The feed concentrations for these measurements were selected to correspond with the concentrations used in the copper extractions reported below. Based on these results, it was concluded that the second half of the contactor could be treated as a differential reactor with no end effects. Samples for chemical analysis were therefore taken at the midpoint and outlet of the reactor, as indicated in Figure 2. By carefully controlling the sampling procedure, it was possible to obtain samples of the aqueous phase which were completely free of organic.

Table I also presents results for the average drop size at different flow rates and organic-phase volume fractions for the reacting copper sulfate-sulfuric acid-Kelex 100 system. A few photographs were also taken when the two phases were pure water and xylene, and these photographs indicate about 25% larger drop sizes in the pure fluid system. The results for $\overline{D}_{32}$ are consistent with measurements made by Middleman (*9*) for several nonreacting, organic dispersed systems in a Kenics mixer. Middleman's results were obtained with dispersed phase volume fractions less than 1%. An experimental value of 11.9

TABLE 1. AVERAGE DROP SIZES IN A KENICS MIXER DURING COPPER EXTRACTION BY KELEX 100

Feed concentrations
Aqueous: 0.01 M $CuSO_4$ and 0.005 M H_2SO_4 in distilled water
Organic: 0.1 M Kelex 100 in xylene

Distance from inlet of reactor (cm)	Total flow rate (ml/s)	Volume fraction organic	N	$\overline{D}_{32}$ (cm)	$\overline{D}$ (cm)	s_D (cm)
8	3.96	0.40	15	0.243	0.152	0.09
27	3.97	0.41	20	0.113	0.094	0.03
43	3.93	0.41	23	0.111	0.085	0.04
61	3.94	0.41	20	0.106	0.096	0.02
61	1.93	0.19	12	0.192	0.168	0.06
61	1.91	0.39	20	0.180	0.149	0.05
61	4.00	0.19	20	0.103	0.089	0.03
61	3.94	0.41	20	0.106	0.096	0.02
61	5.93	0.20	23	0.078	0.066	0.02
61	5.94	0.41	18	0.068	0.062	0.01

$$\overline{D}_{32} = \frac{\sum_{i=1}^{N} D_i^3}{\sum_{i=1}^{N} D_i^2} \qquad \overline{D} = \frac{1}{N}\sum_{i=1}^{N} D_i \qquad s_D^2 = \frac{1}{N-1}\sum_{i=1}^{N} (D_i - \overline{D})^2$$

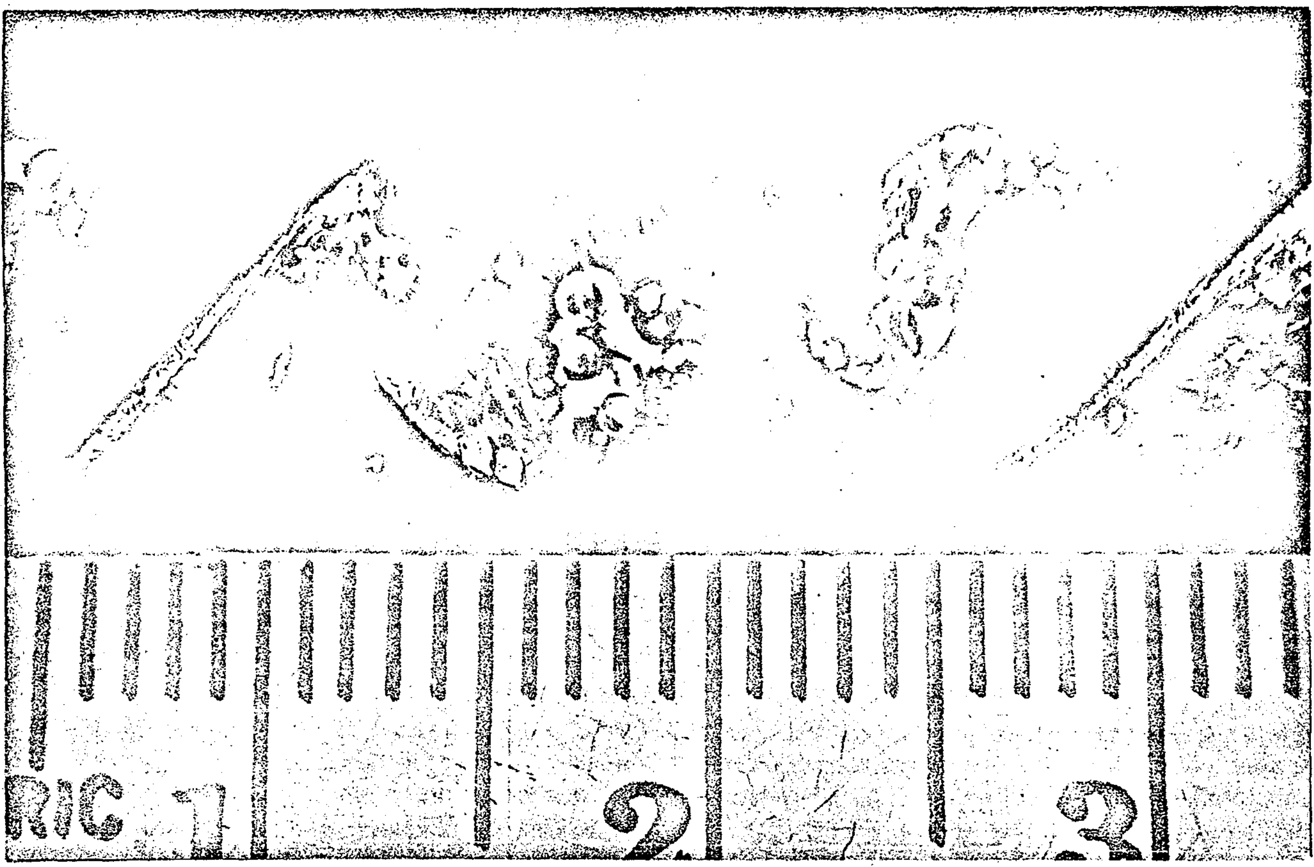


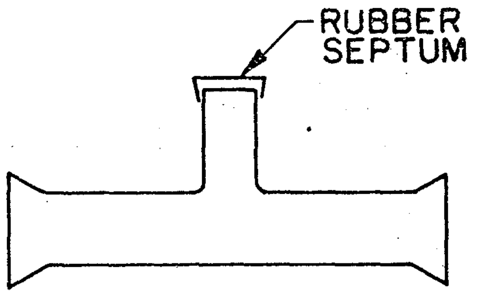
Fig. 3. Photograph of the two-phase system flowing through the reactor.

dynes/cm for the interfacial tension of the copper-Kelex system was used to make the comparison.

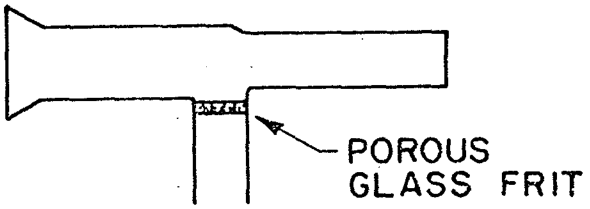
The midpoint and outlet sample fittings are detailed in Figure 4; these fittings were attached to the reactor with standard conical glass couplings. The midpoint samples were taken through a 13 gauge, stainless steel syringe needle that had been tightly packed with glass wool and inserted through the rubber septum shown in Figure 4*a*. A micrometer pipet was used to draw about 1.5 ml of the aqueous phase through the needle during a 2 to 3 min time period. Immediately before a sample was taken, the glass wool packed syringe needle was flushed by using a Cornwall syringe to draw about 1 ml of the aqueous phase through the needle; the holdup volume of the syringe needle is about 0.1 ml. The outlet samples were obtained by adjusting the pressure drop across the settler until the aqueous phase would just flow through the porous glass frit shown in Figure 4*b*. Three to ten milliliters of the aqueous phase could be collected during the time required to draw a 1.5 ml sample at the midpoint. Care was taken to flush thoroughly the glass frit and the short glass tube leading from it before a sample was collected. The midpoint and outlet samples were collected simultaneously.

After both samples had been collected, the midpoint sample was pipetted into an Erlenmeyer flask and the exact volume of the sample noted. The same micrometer pipet was then used to introduce a measured volume of the outlet sample into a second Erlenmeyer. Because of the small sample volumes, it was not possible to rinse the pipet in the usual manner; instead, the pipet tip was carefully washed, rinsed with double distilled water, and dried with AR-grade acetone before a sample was introduced. Replicate analyses showed that this pipet is capable of delivering a 1 ml sample with a standard error of 0.0009 ml; the accuracy is within 0.003 ml.

The small conversions obtained in a differential reactor require high accuracy in the analytical technique if meaningful results are



a) CENTER SAMPLING PORT



b) OUTLET SAMPLING PORT

Fig. 4. Diagrams of the sampling ports.

to be obtained. The small sample size and low copper concentrations used in this application impose especially severe requirements on the analytical technique. The copper concentrations were determined by titration with EDTA using pyrocatechol violet as the indicator (*14*). After the appropriate precautions were applied for EDTA titrations in dilute systems (*7*), the standard error of the analytical procedure was found to be 0.000019 mole/l, based on four replicates. This corresponds to a relative precision of about 0.2% in the range of copper concentrations of interest.

COPPER EXTRACTION WITH KELEX 100 IN A KENICS MIXER

Bauer (*1*) found that the rate of copper extraction from aqueous copper sulfate-sulfuric acid solutions by Kelex 100 in xylene could be correlated with a standard error of about 12% by

$$N_{Cu} = \frac{3.64 \times 10^{-8} c_{Cu}^{0.728} c_{HR}}{(9.54 \times 10^{-3} + c_{H_2SO_4})^{1.58}} \tag{5}$$

where the concentrations are expressed in moles/liter and the flux is in moles/square centimeter second. The data on which Equation (5) is based were taken over the concentration ranges shown in Table 2. The measurements were performed with a growing drop cell; and, as discussed above, we would expect the resulting correlation to be accurate except for a multiplicative constant of order unity. Bauer estimated the activation energy of the reaction to be 12.6 kcal/mole; the above rate expression applies at 25°C.

The fractional copper conversion in a Kenics mixer was measured as a function of total flow rate and volume fraction organic phase for three sets of initial concentrations: $c_{Cu} = 0.01$ and $c_{H_2SO_4} = 0.005$ mole/l, $c_{Cu} = 0.02$ and $c_{H_2SO_4} = 0.005$ mole/l, and $c_{Cu} = 0.01$ and $c_{H_2SO_4} = 0.0005$ mole/l. The concentration of reagent was fixed at 0.1 mole/l for all the experiments. These concentrations correspond to the regions of Bauer's experimental design most likely to be encountered in industrial applications. Distilled water and AR-grade copper sulfate, sulfuric acid, and xylene were used to prepare the feed solutions; the Kelex 100 (lot No. 16133) was of commercial grade and was used as received from Ashland Chemicals, corresponding to the manner in which Bauer's intrinsic rate data were taken. In the calculations, the molecular weight of Kelex 100 was taken to be 311.

TABLE 2. EXPERIMENTAL DESIGN FOR INTRINSIC REACTION RATE MEASUREMENT FOR COPPER EXTRACTION BY KELEX 100 (*1*)

Initial sulfuric acid concentration	Initial copper sulfate concentration 0.005 *M*	0.01 *M*	0.02 *M*
0.0005 *M*		0.0410	
		0.0820	
		0.1640	
0.005 *M*	0.0205	0.0205	0.0205
	0.0410	0.0410	0.0410
	0.0820	0.0820	0.0820
	0.1640	0.1640	0.1640
	0.3280		
0.05 *M*		0.0205	
		0.0410	
		0.0820	
		0.1640	

Each entry is the initial Kelex 100 concentration for a particular run. The initial copper-chelate concentration was fixed at zero.

The data are summarized in Table 3. In Table 3 the column labeled c_{Cu}^{in} refers to the concentration of copper at the midpoint of the reactor. The acid feed concentrations shown in the Table were determined by potentiometric titration with standard sodium hydroxide. The equilibrium conversion for each run is also shown in the table; these conversions were calculated from Bauer's model of the equilibrium data for this system (*2*). Note that in no case did the measured conversion exceed 15% of the equilibrium conversion. The data are recorded in Table 3 in the order that they were taken. Three levels of total flow rate (2, 4, and 6 ml/s) and two levels of volume fraction organic (0.2 and 0.4) are represented. The three levels of flow rate correspond to residence times of 5.6, 2.8, and 1.9 in the differential reactor portion of the contactor.

The chemical analyses for copper concentrations were carried out pairwise; that is, the titrations for the inlet and outlet samples for a particular run were carried out one after the other so that the end point color of the two samples could be readily compared. The appropriate variable to use in constructing models for these data is thus the difference in copper concentration between the inlet and outlet of the reactor:

$$\delta = c_{Cu}^{in} - c_{Cu} \tag{6}$$

It is difficult to obtain an accurate estimate of the overall precision of the experiments because the nature of the equipment makes it impractical to conduct exact replicates. The overall standard error s_δ can be bounded, however, by the standard error estimated from the three near replicates reported in Table 3 and the standard error of the chemical analysis. These calculations give

$$0.00003 < s_\delta < 0.0003 \text{ mole/l} \tag{7}$$

We would expect the true value of s_δ to be appreciably less than the upper limit based on the three near replicates because some of the variation in the near replicates can be qualitatively explained by the small deviations in flow rates and temperatures which were recorded.

The intrinsic reaction-rate model, Equation (5), is considered to be accurate except for a multiplicative constant, say k. Defining an average drop diameter $\bar{D}_{32}$ such that

$$a = \frac{6\phi}{\bar{D}_{32}} \tag{8}$$

and rewriting Equation (2) in terms of δ and the intrinsic reaction rate, we find that

$$\delta = \frac{6\phi}{1-\phi} \tau \frac{k}{\bar{D}_{32}} N_{Cu}(c) \tag{9}$$

TABLE 3. COPPER EXTRACTION WITH KELEX 100 IN A KENICS MIXER

Feed concentrations	Total flow rate (ml/s)	Volume fraction organic	Temperature (°C)	c_{Cu}^{in} (mole/l)	Fractional conversion	Equilibrium conversion
	1.81	0.39	26.0	0.00865	0.057	0.996
	3.94	0.20	29.8	0.00924	0.029	0.933
	5.93	0.41	30.5	0.00861	0.100	0.977
I	3.94	0.40	31.0	0.00866	0.100	0.996
	5.84	0.19	30.9	0.00921	0.034	0.922
	4.05	0.41	30.6	0.00870	0.103	0.996
	2.04	0.22	28.0	0.00922	0.039	0.968
	1.93	0.19	26.3	0.01872	0.010	0.540
	3.95	0.41	27.0	0.01820	0.055	0.976
	1.97	0.41	27.3	0.01777	0.051	0.976
II	6.08	0.21	27.7	0.01899	0.024	0.599
	5.80	0.41	28.0	0.01806	0.048	0.977
	4.01	0.19	28.0	0.01876	0.012	0.551
	3.95	0.20	28.9	0.01885	0.023	0.586
	6.02	0.41	26.3	0.00862	0.133	0.998
	6.03	0.20	26.4	0.00941	0.057	0.958
	4.00	0.19	28.0	0.00950	0.074	0.947
III	1.90	0.42	28.5	0.00797	0.129	0.998
	1.94	0.20	29.5	0.00899	0.032	0.954
	3.98	0.41	31.0	0.00856	0.142	0.998
	5.96	0.40	31.9	0.00853	0.146	0.998

Feed concentrations (mole/l):	Cu	H_2SO_4	HR	CuR_2
I	0.00962	0.00487	0.1	0
II	0.01934	0.00483	0.1	0
III	0.00991	0.000478	0.1	0

for a differential reactor. The intrinsic reaction rate is to be evaluated at the average concentration in the differential reactor and is therefore a function of δ. Thus, the function $N_{Cu}(c)$ is given by Equation (5), with the mean acid and reagent concentrations being computed from the measured copper concentrations the stoichiometry of reaction (1). Equation (9) can be written formally as

$$\delta = \delta(\tau, \phi, c^{in}, T, k/\overline{D}_{32}) \tag{10}$$

The temperature dependence arises through the reaction kinetics.

The factor k may be viewed as a correction factor on the heterogeneous reaction rate which reflects the possibility that the flux in the reactor may differ to some degree from that measured on a single drop. Reactor models can now be constructed by assuming a function form for the dependence of $k/\overline{D}_{32}$ on the independent variables and estimating the parameters in this function by least squares. The parameter estimation was carried out by solving Equation (9) numerically for δ.

A summary of the models which were fit to the extraction data is given in Table 4. The simplest model for the drop size

$$\overline{D}_{32}/k = \theta_1\text{, a constant} \tag{11}$$

is seen to be unsatisfactory. Model 3 arises if we assume

$$\overline{D}_{32} \propto (We)^{\theta_2/2} \tag{12}$$

TABLE 4. SUMMARY OF MODELS TO FIT TO COPPER-KELEX EXTRACTION DATA

Model	Functional form	Parameter values ± ~95% confidence limits	Root mean square residual (mole/l)
1	$\overline{D}_{32}/k = \theta_1$	$\hat{\theta}_1 = 0.278 \pm 0.070$ cm	0.00036
3	$\overline{D}_{32}/k = \theta_1 (Q/4)^{\theta_2}$ Q[=] ml/s	$\hat{\theta}_1 = 0.209 \pm 0.017$ cm $\hat{\theta}_2 = -1.08 \pm 0.19$	0.00013
5A	$\overline{D}_{32}/k = \theta_1 (Q/4)^{\theta_2} (1 + \theta_3 c_{Cu})$ Q[=] ml/s c_{Cu}[=] mole/l	$\hat{\theta}_1 = 0.153 \pm 0.024$ cm $\hat{\theta}_2 = -1.04 \pm 0.14$ $\hat{\theta}_3 = 16.0 \pm 8.6$ l/mole	0.00009

and neglect variation in physical properties. The value of θ_2 estimated from the data indicates that

$$\overline{D}_{32} \propto (We)^{-0.54} \tag{13}$$

This is consistent with the results of several other investigations of noncoalescing dispersions (*15, 3, 13, 4, 9*), who found approximately that

$$\overline{D}_{32} \propto (We)^{-0.6} \tag{14}$$

Although the estimate of the experimental error obtained from the sum of squares for model 3, $s_\delta = 0.00013$ mole/l, is consistent with the estimate based on the near replicates, a plot of the residuals from this model against copper concentration displays a clear trend, the residuals $(\delta_i - \hat{\delta}_i)$ increasing with increasing copper concentration. This trend in the residuals may be indicative of an effect due to changing physical properties, or it may be the result of inadequacies in the intrinsic reaction-rate model. It is not the result of a mass transfer effect: the presence of a mass transfer limitation would tend to decrease the extraction rate at low copper levels relative to the rate at high copper levels, and the trend in the residuals indicates the opposite case. Furthermore, experimental measurements show no discernible effect of copper concentration on the interfacial tension over the range of copper concentrations examined. An attempt to use our conversion data to estimate the value of the exponent for the copper concentration in Equation (5) together with the values of the parameters in model 3 was inconclusive because of the high correlation between θ_1 and the value of the exponent. At any rate, the introduction of a linear term in copper concentration as indicated in model 5A removes this trend from the residuals. In view of the uncertain physical origin of this term, model 5A should not be expected to give meaningful results outside of the range of conditions studied. The residuals from model 5A show no further trends with any of the independent variables.

It is informative to compare values of $\overline{D}_{32}/k$ predicted by model 5A with independent measurements of the drop size. Average drop sizes determined from analysis of photographs of the dispersion are presented in Table 1 and are compared with the predictions of model 5A in Table 5. The feed concentrations given in Table 1 correspond approximately with those for the first set of feed concentrations for the fractional conversion measurements. Therefore, the value of $\overline{D}_{32}/k$ was computed from model 5A by assuming average copper concentrations in the reactor equal to those observed for the corresponding flow rates at the midpoint of the reactor in data set I. In this concentration range, the exact value of the copper concentration has little effect on the computed value of $\overline{D}_{32}/k$.

Comparison of predicted values of $\overline{D}_{32}/k$ with average drop sizes determined from photographic analysis indicates that k has a value of about 0.6. This implies that the average rate of extraction in the flow reactor is roughly one half that observed in the growing drop cell by Bauer (*1*). The standard errors in the drop size measurement indicate an accuracy for $\overline{D}$ of about 2%, and the accuracy of $\overline{D}_{32}$ should be comparable to this value. Furthermore, errors in the drop size measurements resulting from examining a nonrandom sample of drop images would tend to inflate the measured value of $\overline{D}_{32}$, as the natural bias is to overlook the smaller drops. Therefore, the average flux in the flow reactor must be lower than that observed in the growing drop cell.

On the other hand, the functional form of the kinetics given by Equation (5) appears to be consistent with the conversions measured with the flow reactor, particularly with respect to the dependence on acid concentration and temperature. This result and the fact that the flux predicted by Equation (5) is of the correct magnitude establish that the single-drop experiment is a useful tool for isolating the principal chemical aspects of the system from the physical flow behavior of the mixer reactor.

The fact that the kinetic correction factor k is less than 1 may be the result of surface adsorption of an inhibitor for the extraction reaction. Such an effect should become more important as the rate of generation of fresh interface decreases, and it appears reasonable to assume that the surface-generation rate in the flow reactor is less than in the growing drop cell. This assumption is supported by the correspondence of our results for the dependence of drop size on flow rate with drop size measurements made in noncoalescing dispersions. If this is in fact a proper interpretation, one would expect the correction factor to approach 1 as the flow rate through the reactor, and hence the rate of coalescence and redispersion increases. This trend is indicated qualitatively by the results in Table 5.

TABLE 5. COMPARISON OF MEASURED DROP SIZES WITH PREDICTED VALUES OF $\overline{D}_{32}/k$

Total flow rate (ml/s)	Volume fraction organic	Assumed copper concentration	$\overline{D}_{32}/k$ predicted by model 5A (cm)	$\overline{D}_{32}$ from photographic analysis (cm)	$\dfrac{\overline{D}_{32}\text{ (measured)}}{\overline{D}_{32}/k\text{ (model 5A)}} = k$
1.93	0.19	0.00922	0.375	0.192	0.51
1.91	0.39	0.00865	0.376	0.180	0.48
4.00	0.19	0.00924	0.176	0.103	0.59
3.94	0.41	0.00866	0.177	0.106	0.60
5.93	0.20	0.00921	0.117	0.078	0.67
5.94	0.41	0.00861	0.115	0.068	0.59

It is clear from these experiments that the Kenics mixer is an efficient reactor for solvent extraction of metals. Not only were appreciable conversions, as high as 15%, achieved in short residence times, about 2 s, but also the conversions were observed to increase with throughput because of the increased interfacial area; Also, the mixer did not appear to generate very small drops in the range of flows studied so that emulsion formation was avoided. Coalescence occurred very rapidly in the outlet line leading to the settler. Work is continuing to extend these studies to longer reactors and higher conversions.

SUMMARY

The liquid-liquid extraction of metals frequently involves the occurrence of a multicomponent heterogeneous reaction. The intrinsic reaction rate for this reaction can be successfully measured with a growing drop cell, and the results of these measurements can be combined with conversion measurements made in a differential reactor to arrive at a characterization of the reactor which is suitable for equipment design purposes. Such a procedure should provide for a more efficient use of experimental effort than would result from either an overall measurement of rates in process equipment or an attempt to model in a more detailed fashion the physical phenomena occurring within the reactor.

The Kenics mixer appears to be a reasonable alternative to conventional stirred-tank reactors for carrying out metal extractions which are limited by slow chemical kinetics. For the extraction of copper from copper sulfate-sulfuric acid solutions by Kelex 100 in xylene, the mixer can be characterized in terms of a ratio of average drop size to an effective reaction-rate constant ($\overline{D}_{32}/k$).

ACKNOWLEDGMENT

M. E. Tunison was supported by a National Science Foundation Graduate Fellowship. This work has also been funded in part by the National Oceanic and Atmospheric Administrations Office of Sea Grant, Department of Commerce, through an institutional grant to the University of Wisonsin. Kenics Static Mixers® have been supplied by Dr. S. J. Chen of Kenics Corporation.

NOTATION

a = interfacial area per unit dispersion volume, cm^{-1}
c = vector of concentrations
c_i = concentration of species i, mole/l
c_{Cu}^{in} = copper concentration at the inlet to the differential reactor, mole/l
c_{Cu}^{out} = copper concentration at the outlet of the differential reactor, mole/l
c_M = metal concentration
D = drop size, cm
$\overline{D}_{32}$ = an average drop diameter defined so that $a = 6\phi_d/\overline{D}_{32}$, where ϕ_d is the dispersed-phase volume fraction. For spherical drops, $\overline{D}_{32} = \Sigma D_i^3/\Sigma D_i^2$
k = correction factor on the heterogeneous rate constant, or an effective rate constant, dimensionless
L = length of reactor, cm
N = number of drops counted
N_i = flux of species i, mole/cm^2 · s
N_M = flux of metal out of aqueous phase, mole/cm^{2}s
R = tube diameter, cm
T = temperature, °K
We = Weber number, $2Rv^2\rho/\sigma$
z = distance from entrance, cm

GREEK LETTERS

$\delta = c_{Cu}^{in} - c_{Cu}^{out}$, mole/l
ζ = dimensionless reactor length, z/L
θ_i = parameter in reactor model
ϕ = organic-phase volume fraction
ρ = density, g/cm^3
σ = surface tension, dyne/cm
τ = residence time, $SL/Q = L/v$, s

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